Photoacoustic Spectroscopy of Pressure- and Temperature-Dependence in the O_2 A-Band

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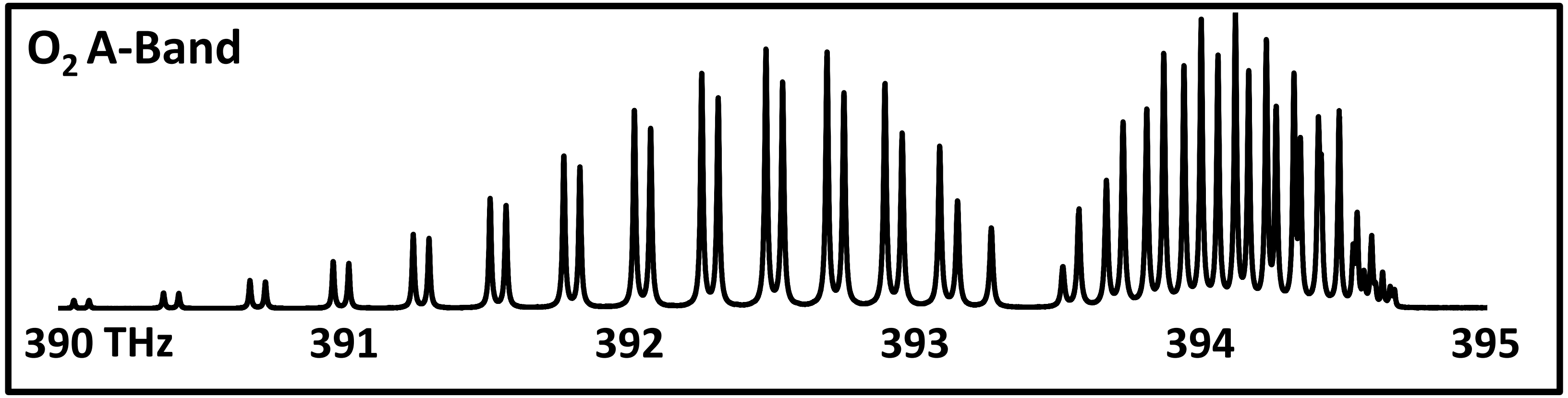
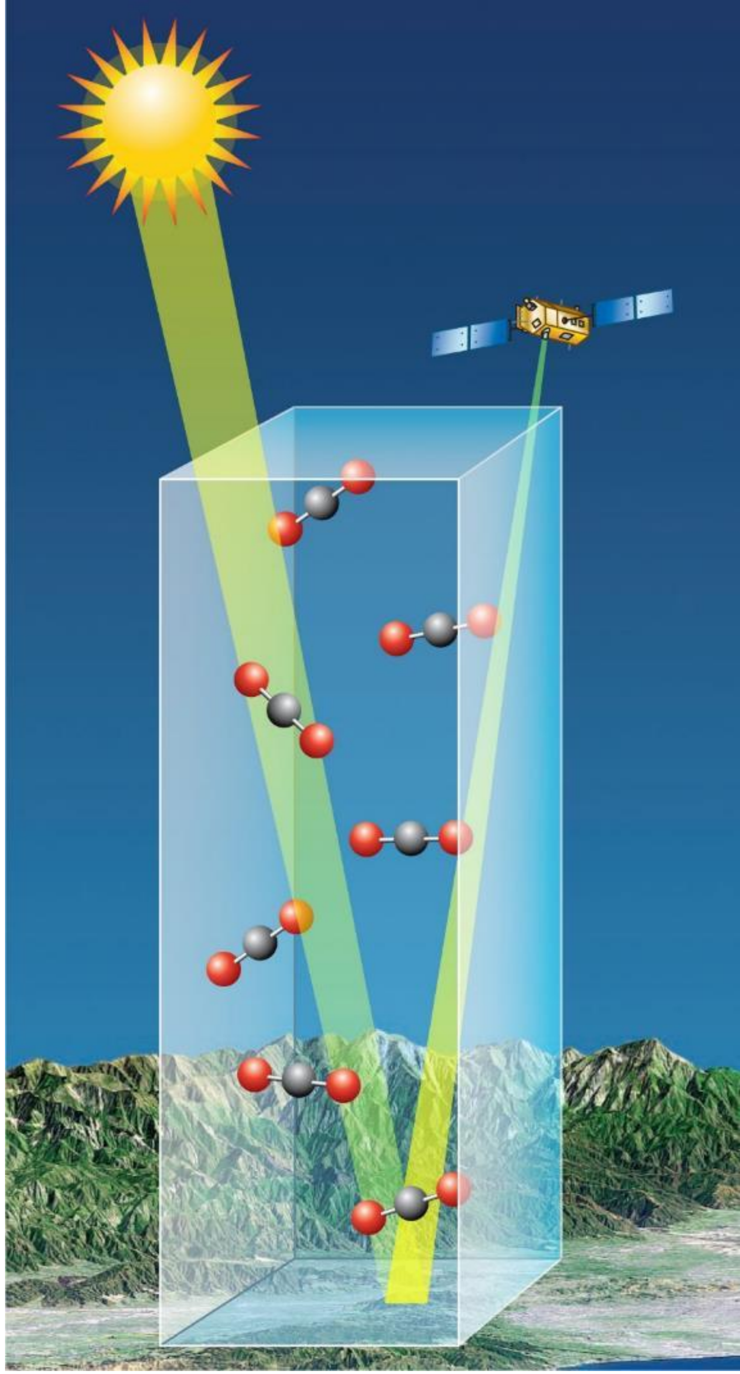
OCO-2 Oxygen Requirement

- OCO-2 requires accurate spectroscopy (0.1%) in the O_2 A-Band
- Drouin et al. study[1] resulted in ~0.5% accuracy
- Line Mixing (**LM**) and Collision Induced Absorption(**CIA**) have effect ~1% and are leading contributors to remaining issues





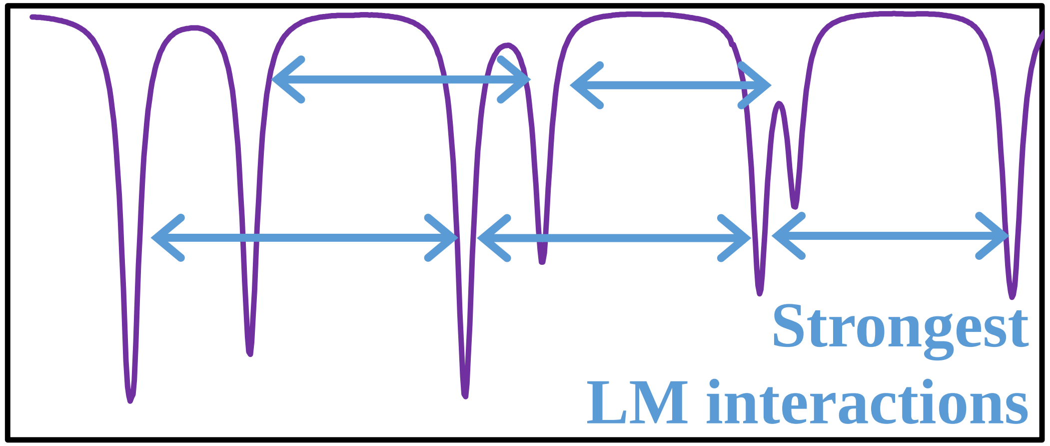
oco.jpl.nasa.gov/images/ocov2/OCO_column.jpg

[1]Drouin et al. DOI: 10.1016/j.jqsrt.2016.03.037.

Line Mixing and Collision- Induced Absorption

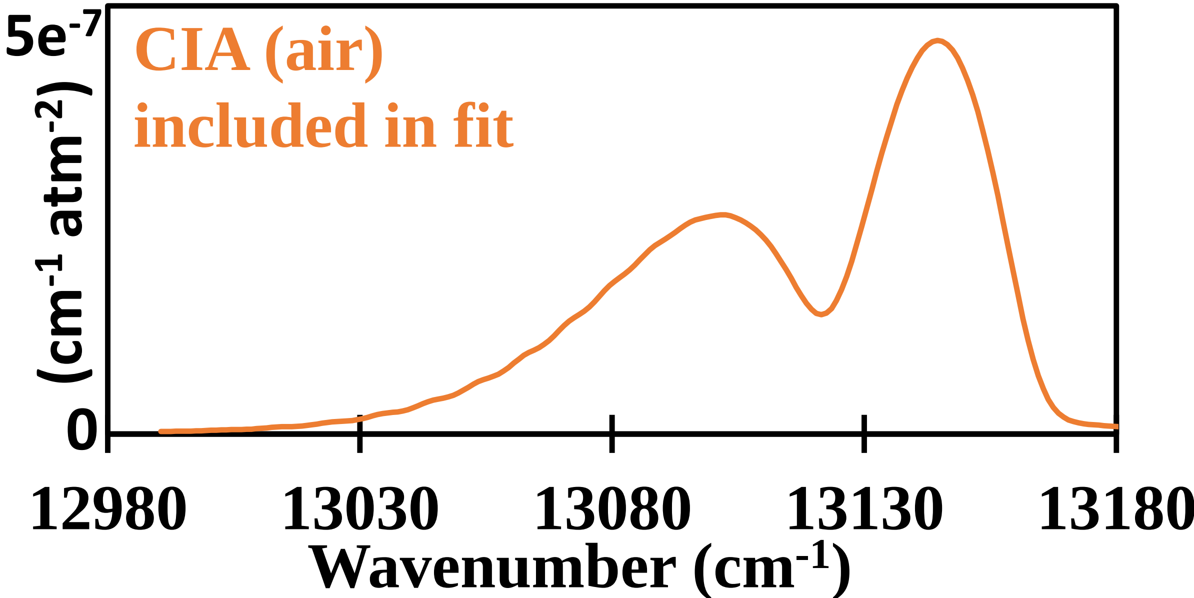
Line Mixing (LM)

When two nearby lines have interacting quantum levels, stronger lines will steal intensity from weaker lines, and both become asymmetric.



Collision Induced Absorption (CIA)

Weak ‘continuum’ absorption underneath the A-band caused by collision-allowed transitions.



An Experiment Designed to Measure LM and CIA

Photoacoustic Spectroscopy Advantages

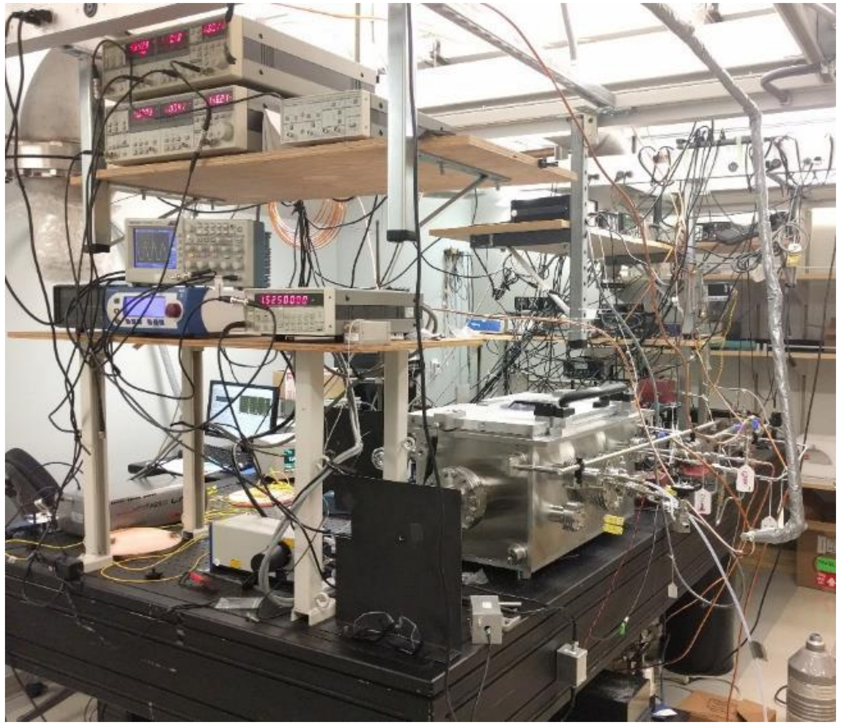
- **Zero baseline**: Ideal for measuring LM/CIA
- **Large dynamic range:**

  <100 Torr to >4 atm. without saturating

Ultimate Goals:

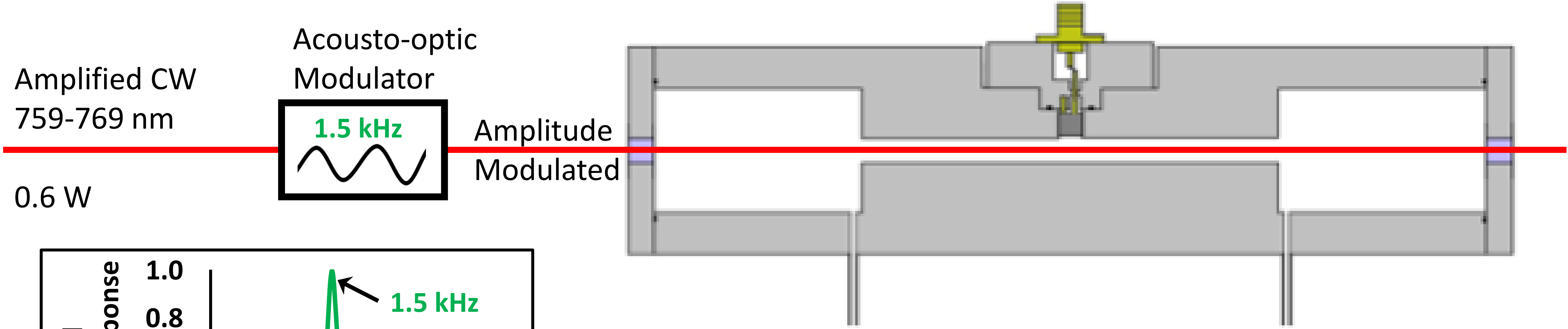
- High frequency resolution measurements over full A-Band
- Atmospherically relevant temperatures

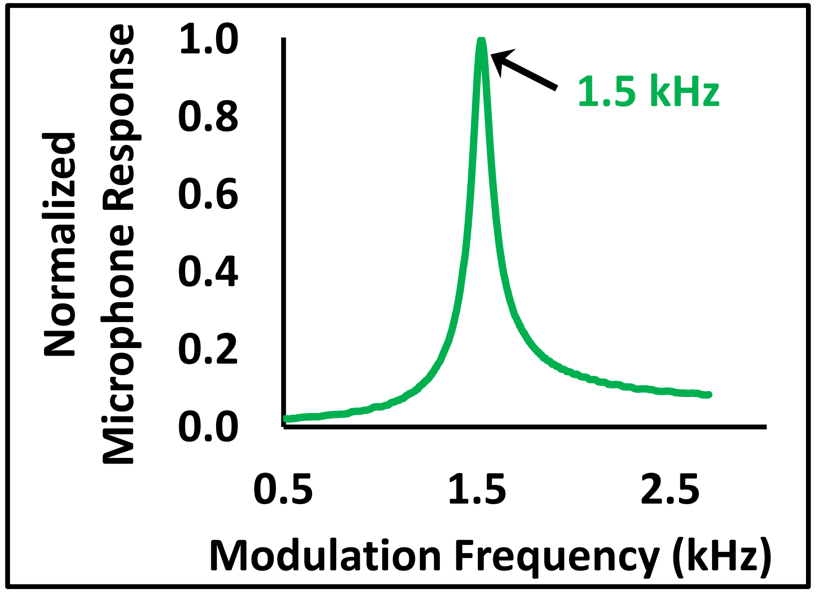
  ~220 K- 296 K



LM and CIA have >1% effect on satellite retrievals and must be better characterized using new laboratory data.

Photoacoustic Resonator





absorption →thermal expansion →pressure wave → sound

Photoacoustic signal depends on:

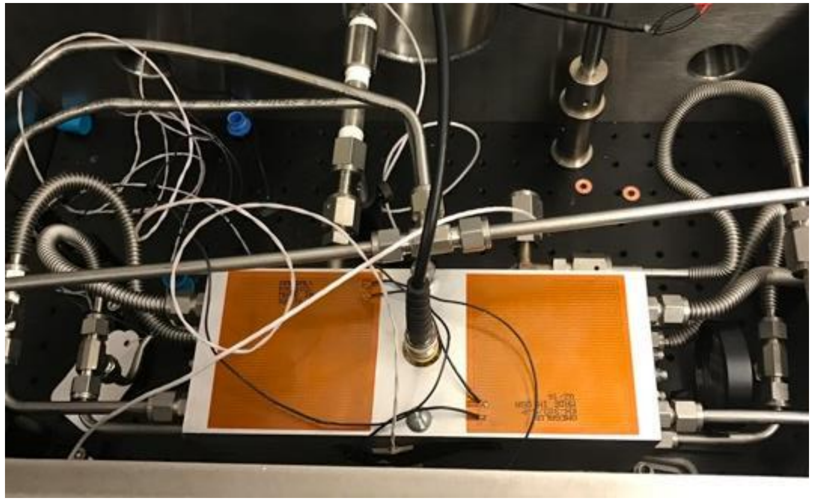
- response function dependent on microphone properties, resonator shape, and gas composition
- absorption quenching efficiency
- modulated laser power

Cell design: Gillis, Havey, Hodges, *Rev. Sci. Instrum.* 81, 064902 (2010)

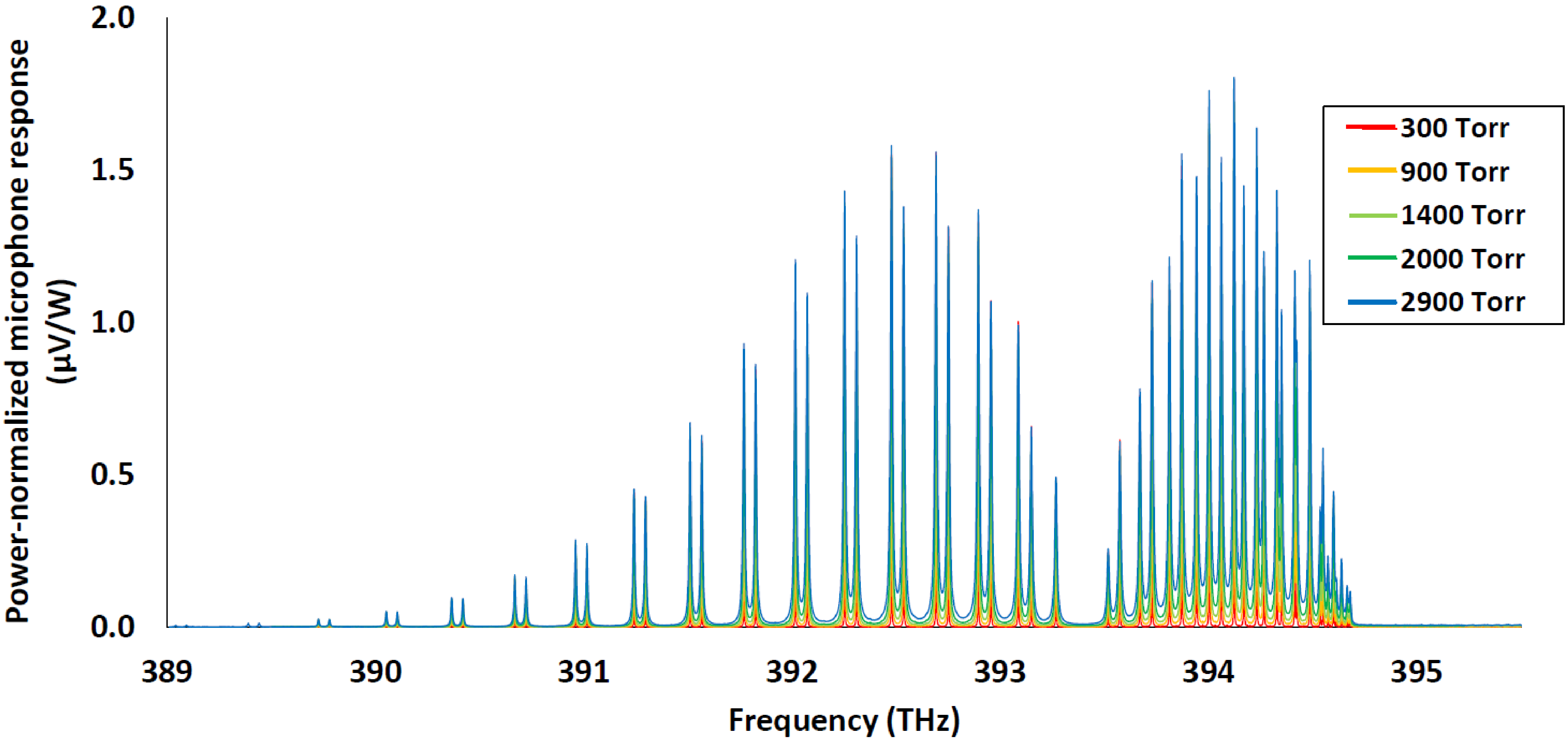
Spectrometer Properties

- Modehop- free scanning across 5+ THz A-Band
- 2 MHz frequency resolution: WLM calibrated with stabilized HeNe
- ~1 day-long scans with evenly spaced points
- Pressure range: ~100-3000+ Torr
- Temperatures: Stability at 0.6 K over 1 day
  - Planned lower temperature measurements 193 – 296 K (microphone limited)

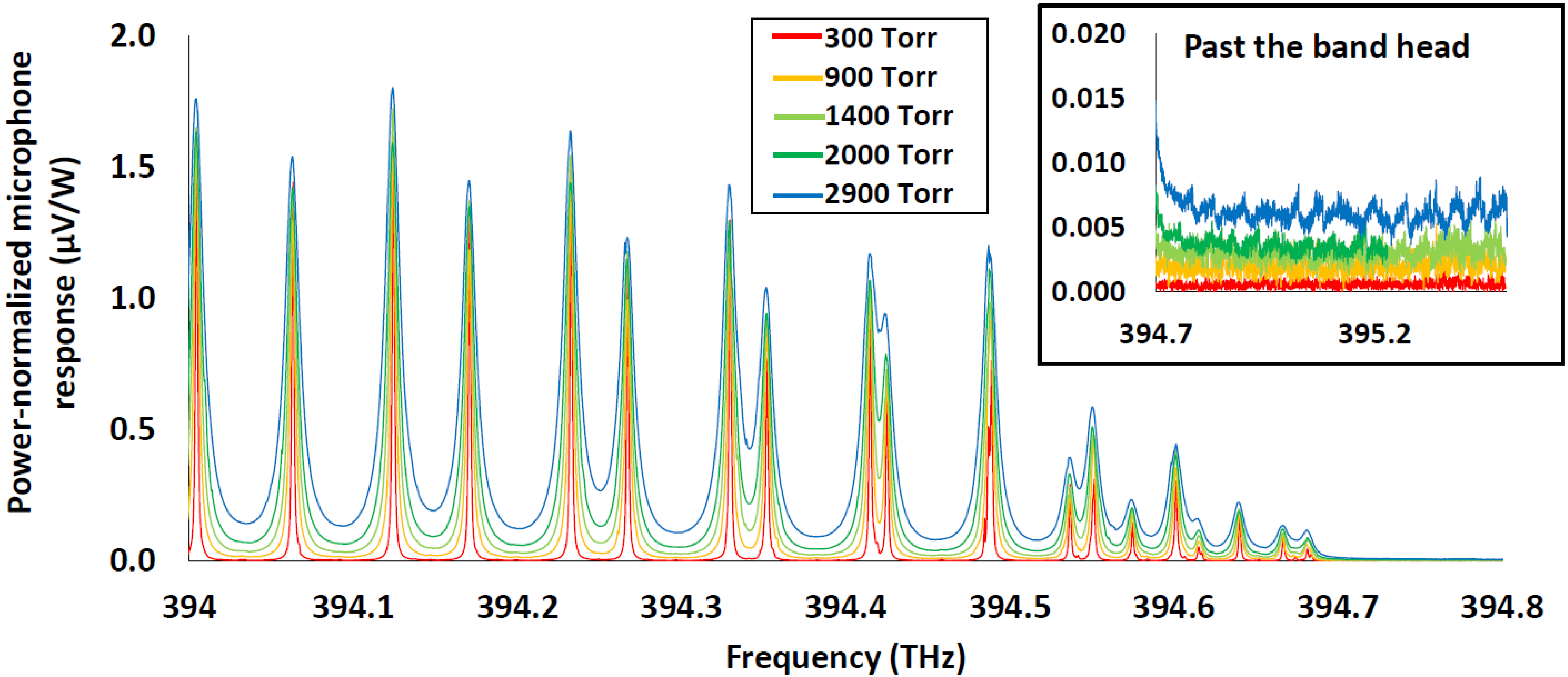
→



Photoacoustic spectra of Pure O2, 296 K



Band head region



Analysis Overview

- Analysis done with Labfit multispectrum fitting software
  - Speed-Dependent Voigt with Line Mixing and CIA
- Will compare to Drouin et al.'s fit:
  - Line Mixing: separate matrices for self- and foreign- gasses, P- and R- Branch,
    - Splitting between doublets has been neglected
    - Matrices are fixed to theory except for matrix-wide scaling factors
  - CIA:
    - Determined by empirical fit to TCCON spectra (ground-based FTS measurements of the atmosphere)

Comparison to previous dataset

Pure O_2 in published A-Band fit

Technique	Pressure (Torr)	Temp (K)
CRDS	1	295
FTIR	200	297
FTIR	503	298
FTIR	415	205
FTIR	794	207
FTIR	721	189
FTIR	1000	189

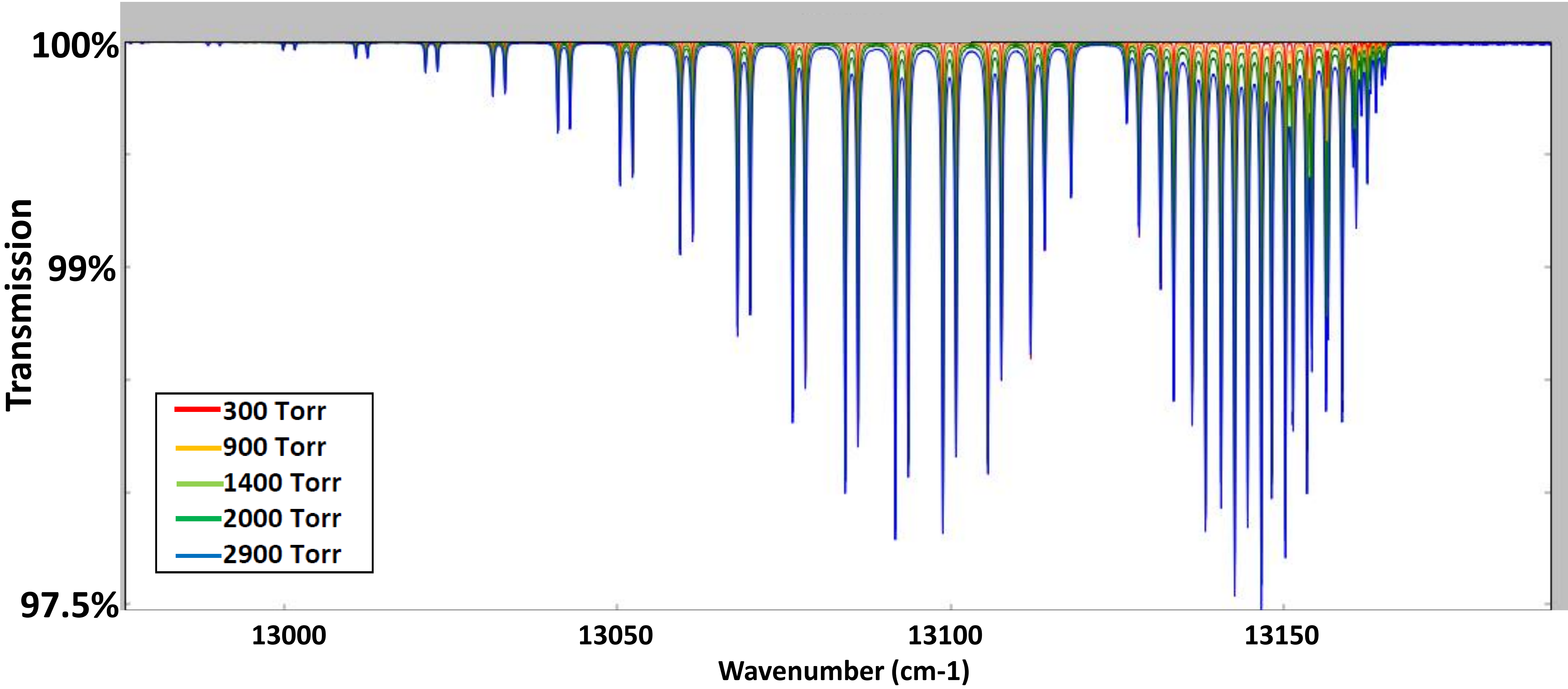
Pure O_2, PAS

Pressure (Torr)	Temp (K)
309	297
500	297
901	297
1404	297
2036	297
2894	297

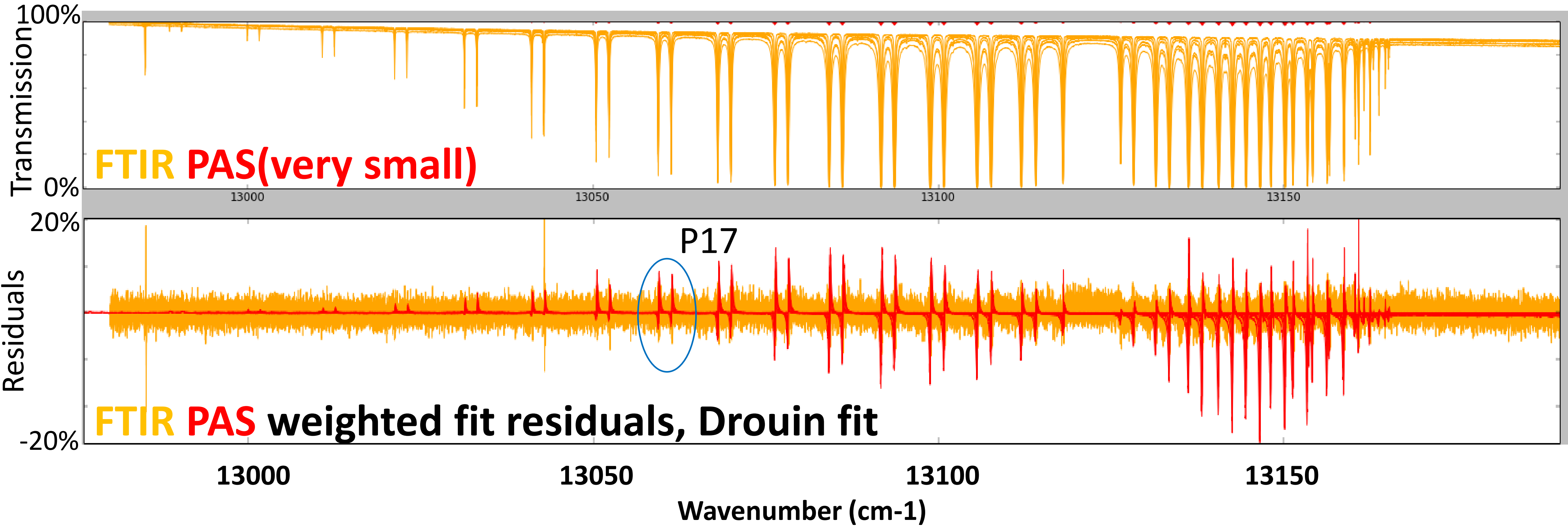
- PAS spectra will be added to existing fit
- PAS will benefit from intensity constraints to FTIR/CRDS data
- FTIR/CRDS will benefit from zero baseline and high pressure of PAS

Spectrum of Pure O_2 in Transmission

Transformed from PAS signal to % transmission: strongest lines are 98% transmission

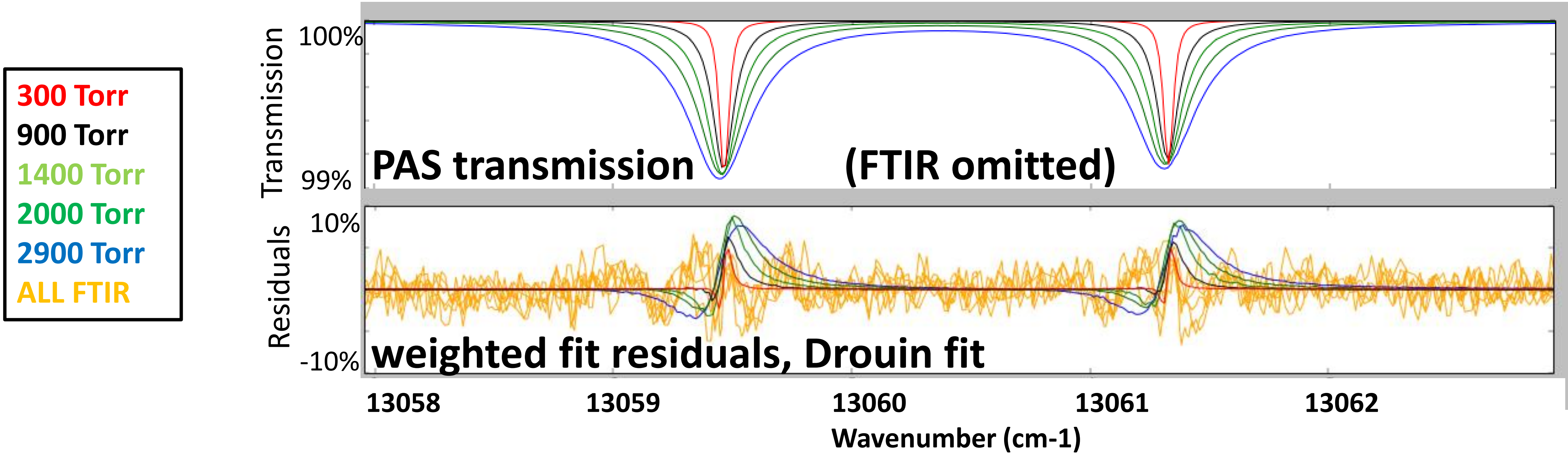


FTIR and PAS Datasets: Fit of PAS Spectra to Drouin parameters lead to significant residuals



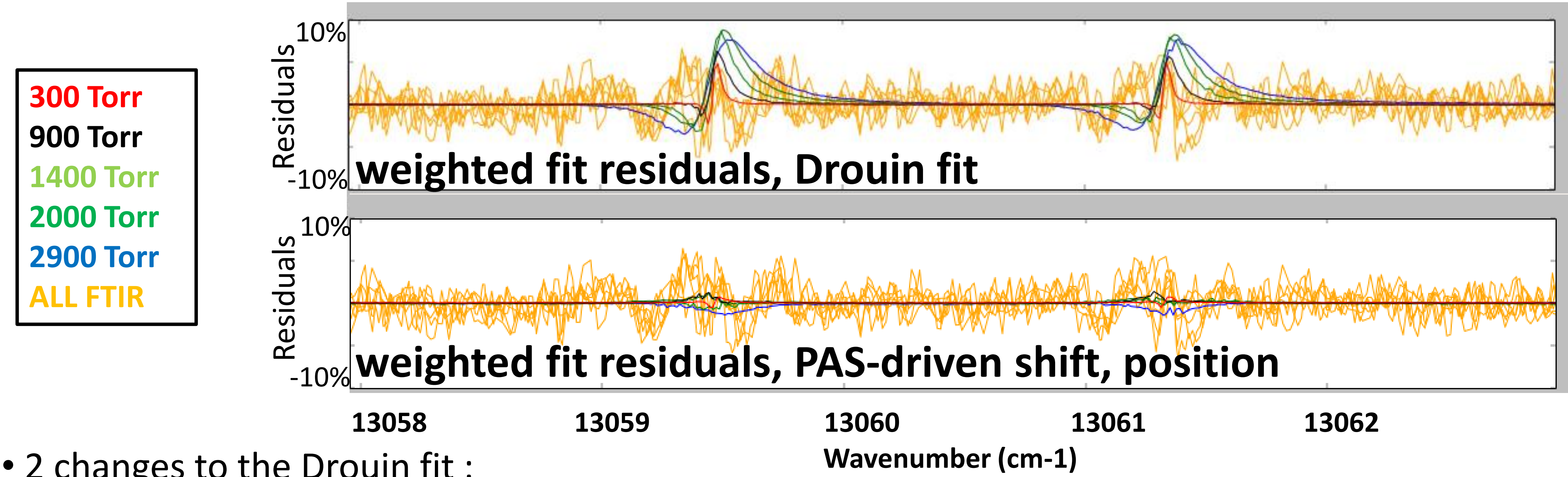
- FTIR and PAS residuals are weighted by maximum absorption (PAS 2%, FTIR 100%)
- PAS noise levels are much lower but there are systematic residuals at each peak
- Will focus on P17 doublet for a preliminary look at what we can learn

Largest PAS residuals are frequency-related



- Pressure shift is a major contributor to the PAS residuals, clear pressure trends (band-wide)
- Absolute position is also a factor:
  - Drouin fit has mild disagreement with HITRAN2012 and HITRAN2016 (~5-10 MHz)

Adjusting self pressure shift improves PAS fit

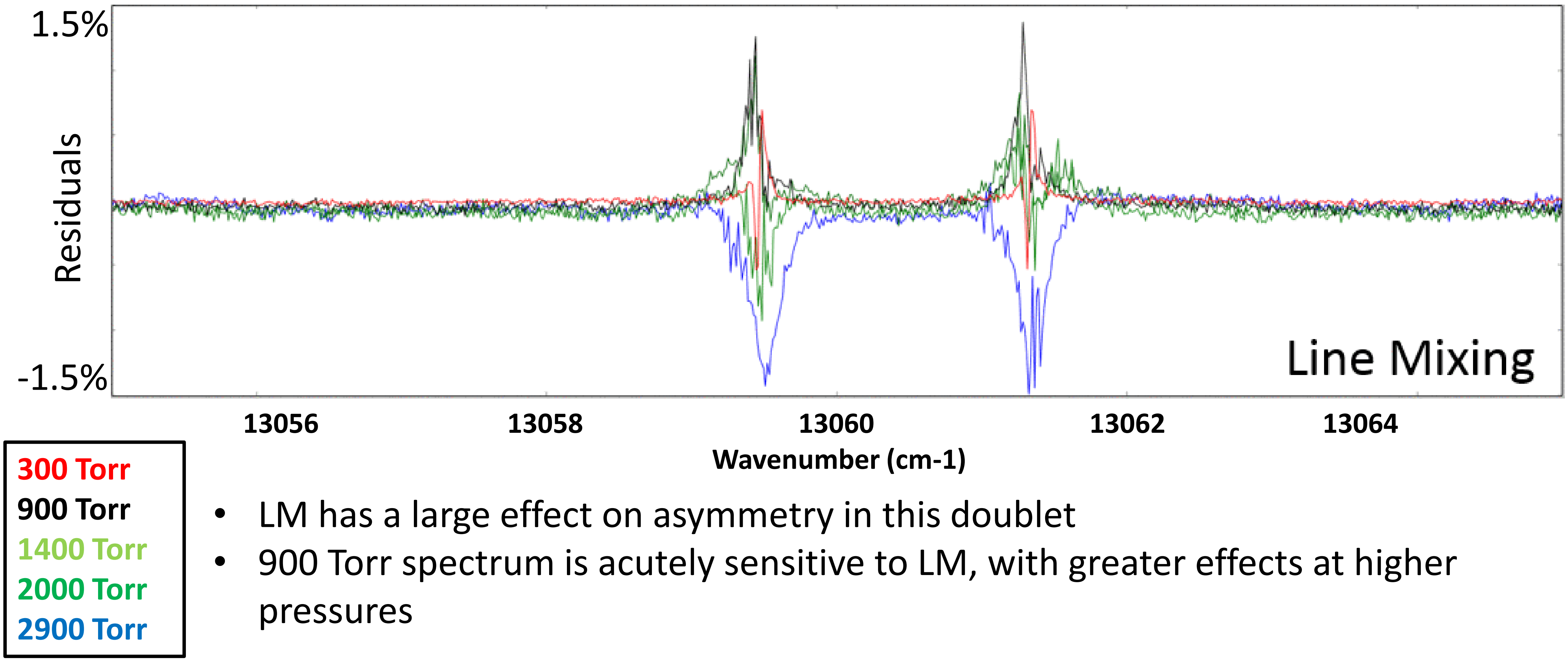


- 2 changes to the Drouin fit :
  1. PAS data was fit for self-shift, this shift was applied to the global fit
  2. FTIR calibration was frequency offset to match PAS, FTIR residual structure unchanged

- Line position WAS NOT changed from Drouin fit, and is not a perfect match
- Majority of remaining PAS residual structure is due to intensity effects, LM, and CIA.

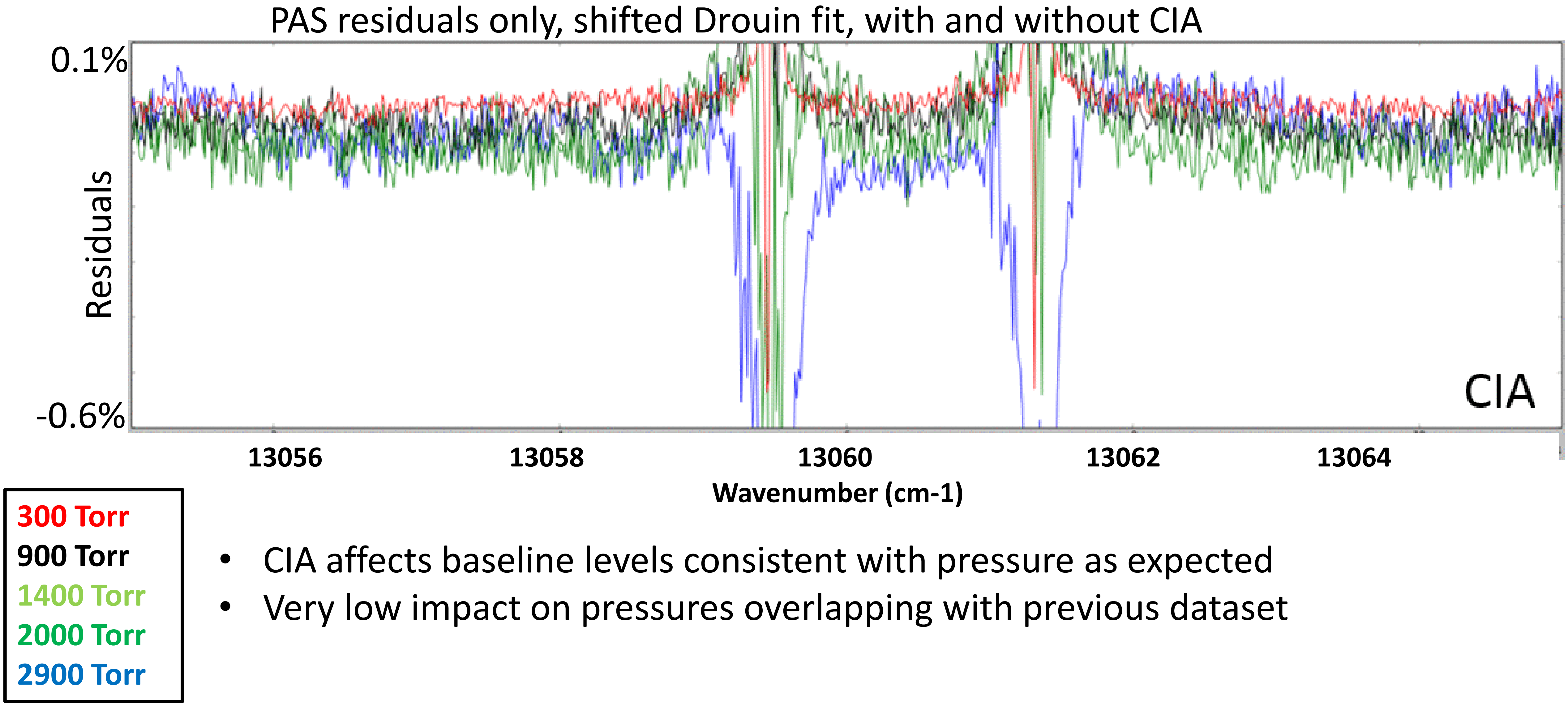
Is PAS Sensitive to Line Mixing?

PAS residuals only, shifted Drouin fit, with and without Line Mixing



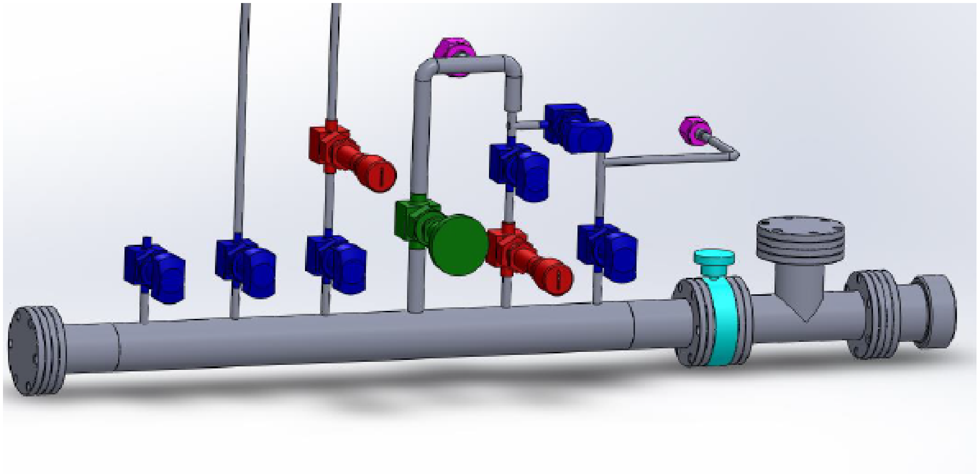
- LM has a large effect on asymmetry in this doublet
- 900 Torr spectrum is acutely sensitive to LM, with greater effects at higher pressures

Is PAS Sensitive to Collision-Induced Absorption?



- CIA affects baseline levels consistent with pressure as expected
- Very low impact on pressures overlapping with previous dataset

Gas mixing manifold design, to be attached to PAS resonator



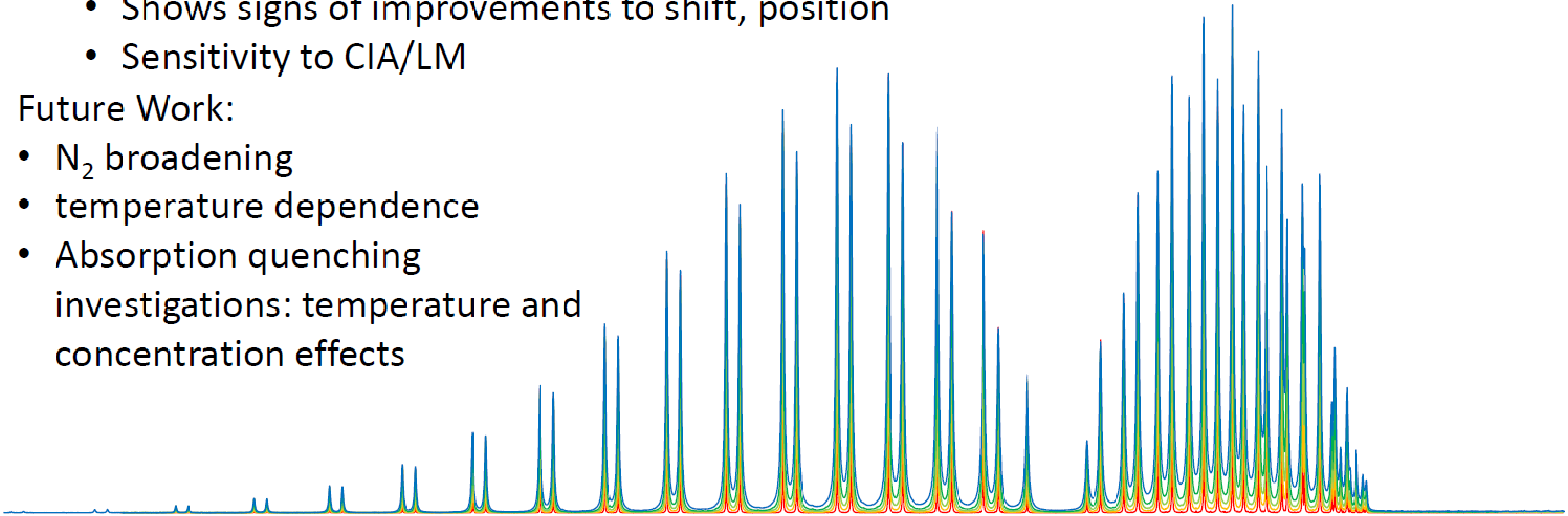
Summary

Accomplishments:

- PAS spectrometer developed and acquiring data
- Pure O2 room temperature is almost complete
- PAS analysis has begun
  - Shows signs of improvements to shift, position
  - Sensitivity to CIA/LM

Future Work:

- N_2 broadening
- temperature dependence
- Absorption quenching investigations: temperature and concentration effects



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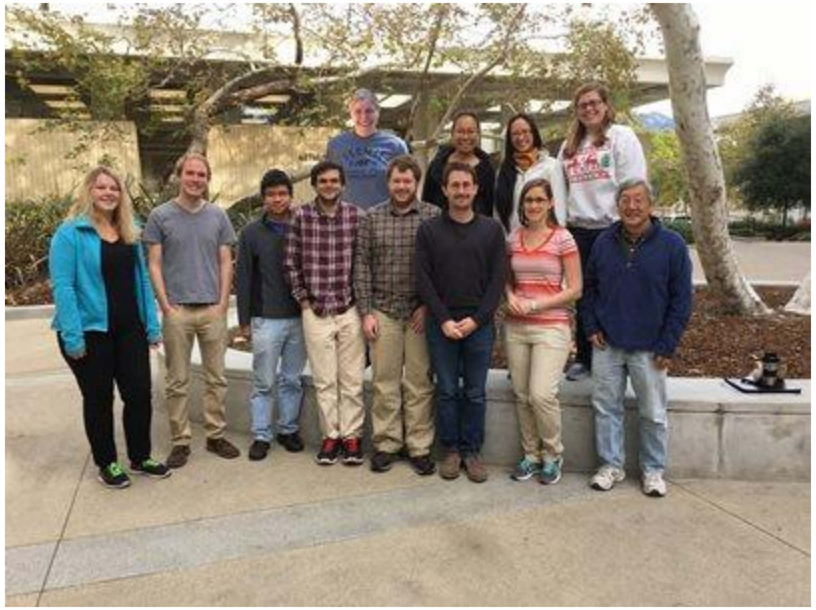

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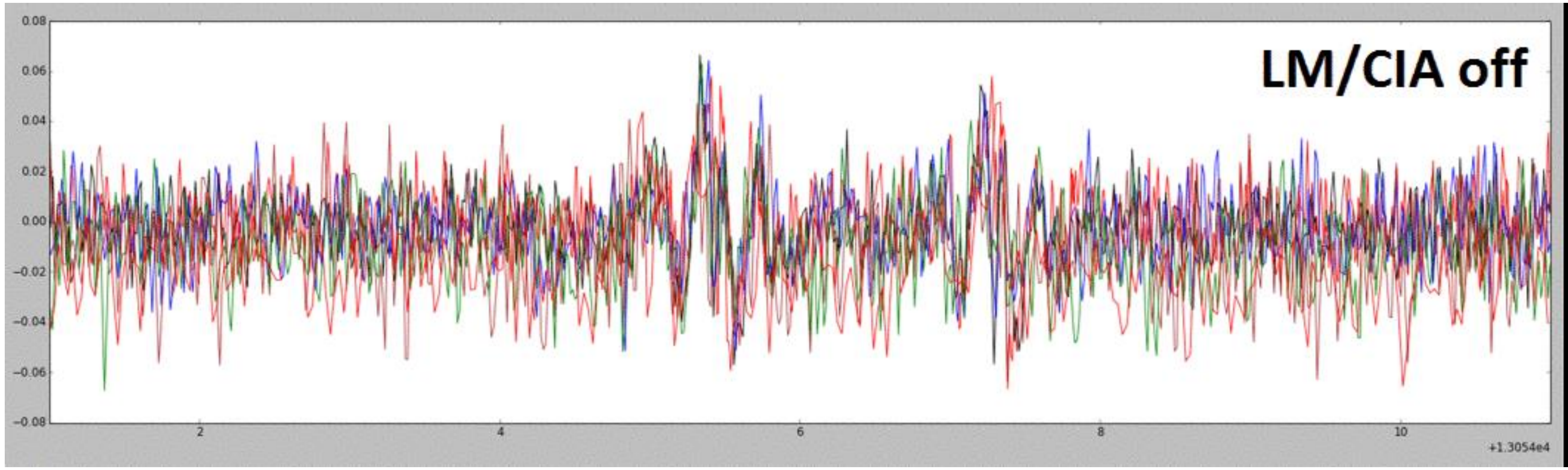
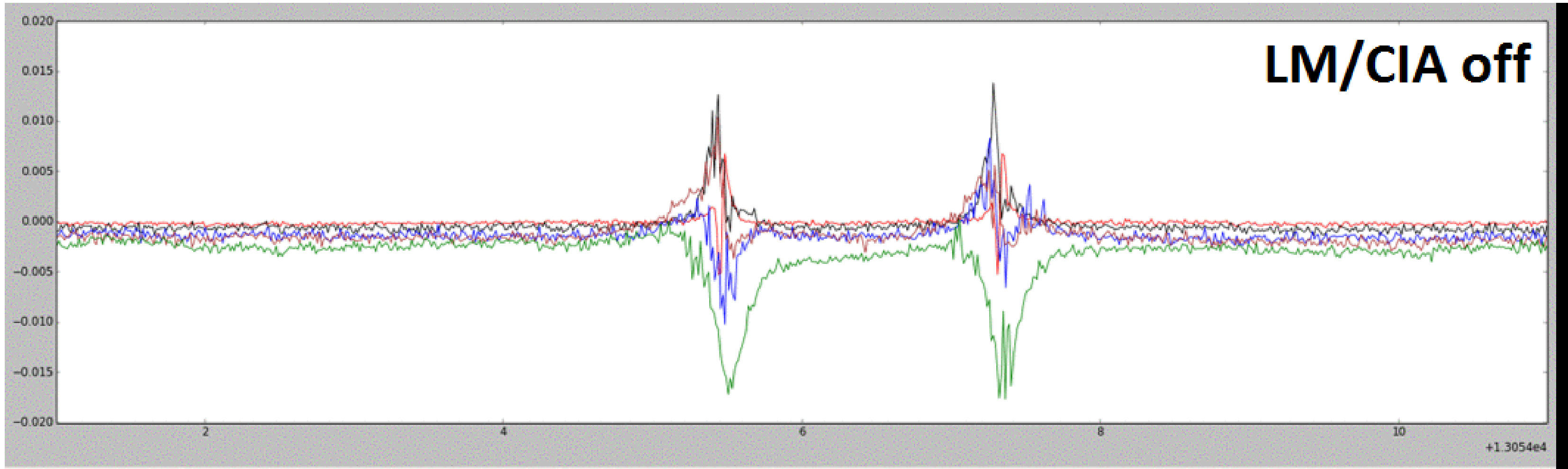
Line Mixing and Collision-Induced Absorption

- FTIR noise is very close to the level of the CIA and LM effects on the spectra.
- PAS noise is much lower and especially the high pressure spectra are very sensitive to both LM and CIA



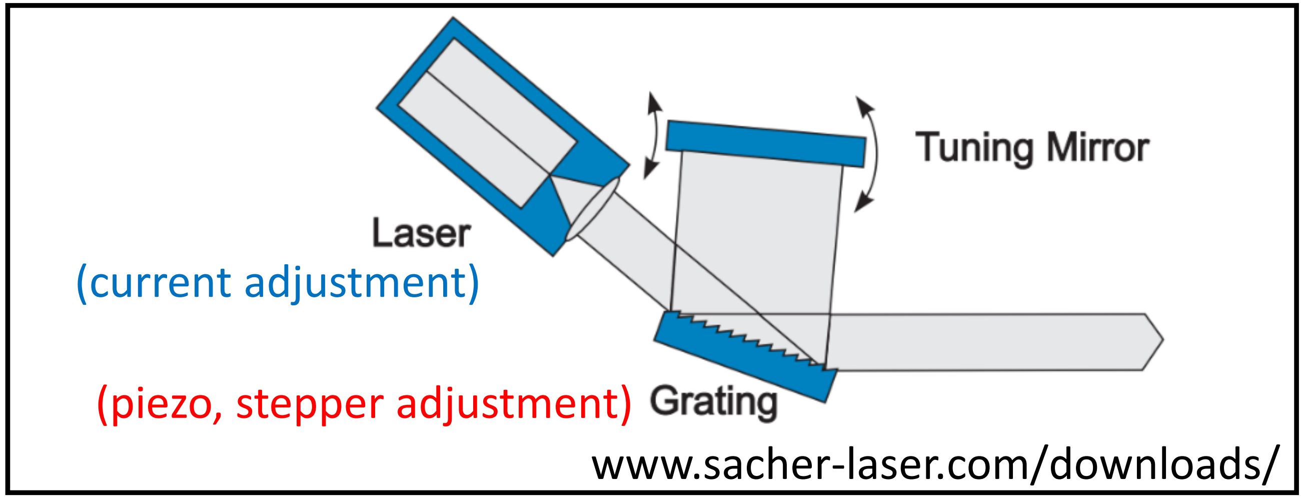


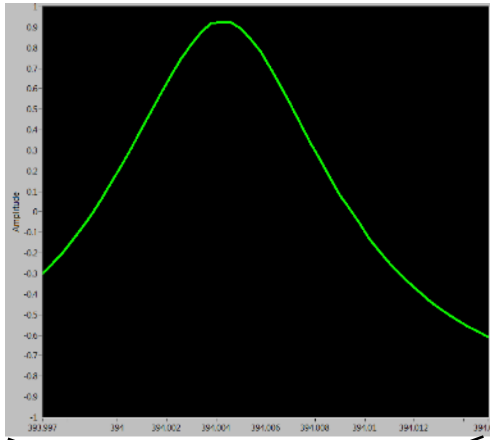
Frequency Scanning

- Scans have constant step size, currently 400 MHz
- Modehops (cavity mode/grating mismatch) avoided by adjusting laser current
- Scanning software uses current, piezo, and stepper to collect full A-Band

Laser current: ~100 MHz Range
<50 kHz precision

Piezo: 18 GHz Range
2 MHz precision

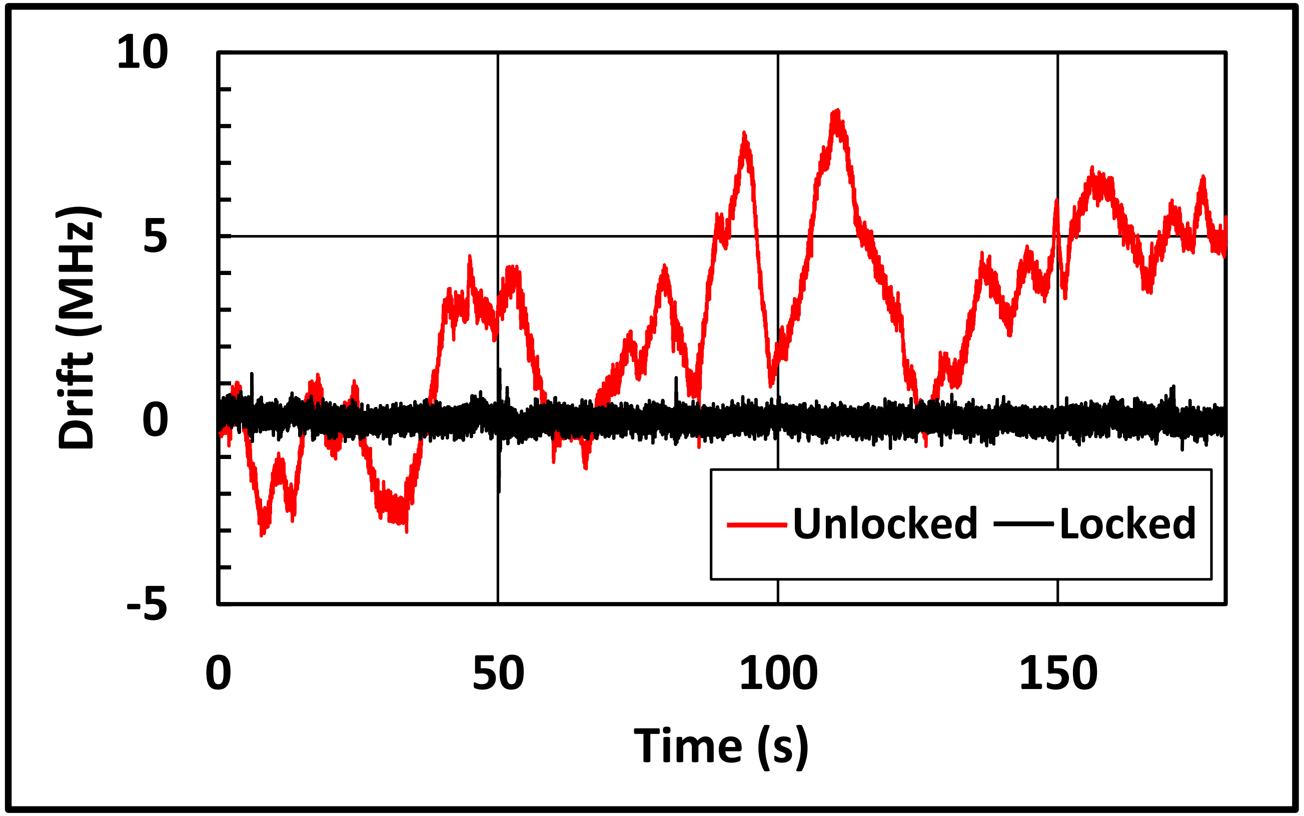




Stepper motor: 5+ THz Range, GHz precision

Frequency Stability

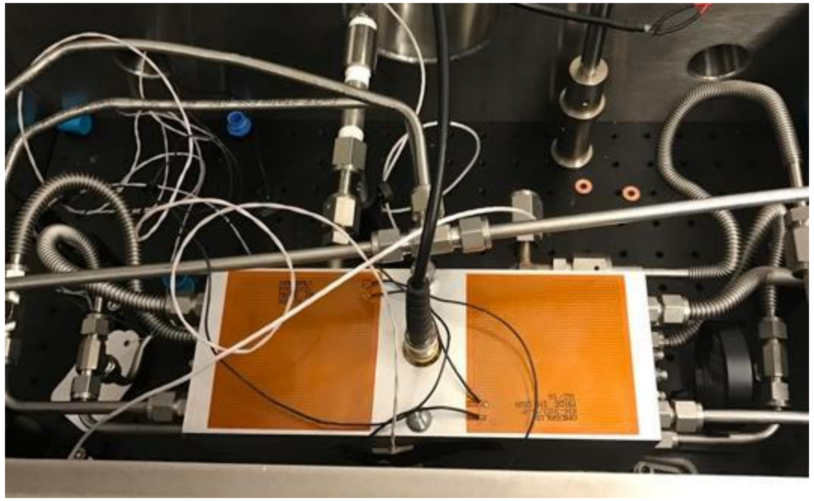
HighFinesse Wavemeter
- Calibrated with stabilized He-Ne
- 2 MHz accuracy
- 120 Hz+ scan rate



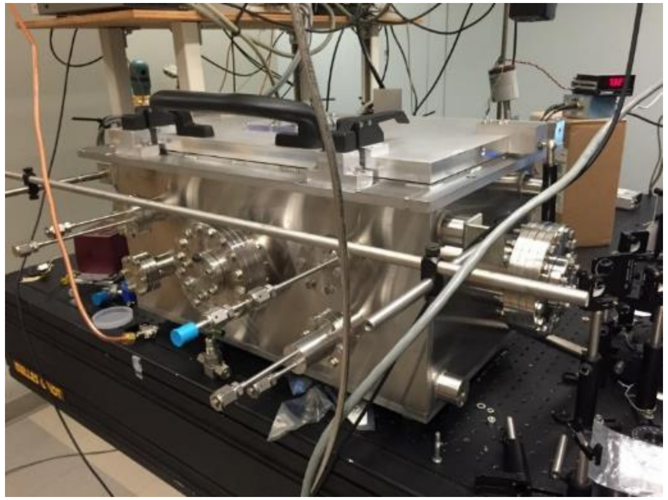
- Laser current is modulated at 120 Hz to lock to targeted λ-meter reading
- 0.5 s averaging, <2 MHz standard deviation

Temperature control plans

Resonator



Temperature control housing
Targeted range: 220 K-296 K
Targeted stability: >1 K
(Still in development, 0.6 K achieved over 5 hrs at 282 K)



Vacuum chamber
Room T, no stabilization:
0.6 K in 24 hrs drift
(currently achievable)

Fitting Photoacoustic Spectra

Labfit used to ultimately include this data in the larger A-band multispectrum fit

$$100 * e^{-\overbrace{\boxed{Mic.\,response}}^{\text{Measurement}} * S.F.} = \overbrace{\boxed{T(\omega)}}^{\text{Labfit Input}} = \overbrace{\boxed{B * e^{-S(T)\,N\,L\,\Gamma(\omega)}}}^{\text{Fit Parameters}}$$

- S.F. Scale Factor depends on cell constant and quencher efficiencies
  - For current measurements empirically determined for ~99% transmission
- L Pathlength: correction factor to match predetermined S(T) in our fit
- B Baseline: fixed to 100% transmission based on low- pressure scans
- $\Gamma(\omega)$ Line shape model: Labfit's Speed-Dependent Voigt